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OFFICE OF
CHEMICAL SAFETY AND
POLLUTION PREVENTION

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MEMORANDUM

SUBJECT: Analysis of PFAS in selected mosquito control products from the Maryland Department of Agriculture.
ACB Project # B21-19

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EXECUTIVE SUMMARY

As requested by the Maryland Department of Agriculture (MDA), the EPA Biological and Economic Analysis Division (BEAD) Analytical Chemistry Branch (ACB) Laboratory in Fort Meade, MD analyzed three (3) samples of mosquito control products: two samples (duplicate) of Permanone 30-30 (EPA Reg. No. 432-1235) and one sample of PermaSease 30-30 (EPA Reg. No. 53883-459-86291), for presence of per- and polyfluoroalkyl substances (PFAS). To have as controls for a comparative analysis to the MDA samples, the ACB obtained directly from the manufacturer of Permanone 30-30 a retained sample from a lot produced nine (9) days after the lot purchased by MDA, and three (3) samples taken from different points along a recent Permanone 30-30 production line and storage. Details of the products samples received and analyzed are listed

in **Table 1**, along with blank control samples (one (1) unused sample container from MDA; and one (1) unused sample container and a production field blank from the manufacturer). Twenty-eight (28) PFAS compounds are targeted in this analysis and are listed in **Tables 2 - 4**.

Using the ACB method for analyzing PFAS in oily matrices (see **Appendix I**), one PFAS compound (PFHpA (Per-fluoro-heptanoic acid)) was initially identified in all three (3) MDA samples (Permanone 30-30 and PermaSease 30-30) and the retained sample from the manufacturer, but not in the three (3) Permanone 30-30 samples from a recent manufacturer's production lot, nor in the rinsate samples from the unused containers (MDA sample container and manufacturer's 5-gal container). This ACB method was modified from the EPA Method 537.1¹ and was based on the use of a liquid chromatography tandem mass spectrometer (LC-MS/MS). However, further testing of these samples using a Q-Exactive™ HF high resolution accurate mass (HRAM) mass spectrometer coupled with liquid chromatography (HRAM LC-MS) did not confirm the presence of PFHpA. The PFHpA peak initially identified in the LC-MS/MS analysis for the MDA samples and the retained sample is, therefore, believed to be a false positive resulting from possible matrix interference.

The ACB concludes that none of the targeted PFAS compounds are detected in the MDA PermaSease 30-30 sample and the two MDA Permanone 30-30 samples, nor in any of the product samples received directly from the manufacturer, at or above our method limit of detection (LOD estimated at 0.008 ppb). All blank control samples are also free of target analytes.

¹ https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL

INTRODUCTION

The BEAD/ACB laboratory was requested by the MDA to analyze three (3) oil-based pesticide product samples for presence of PFAS. This included two Permanone 30-30 samples (duplicate) and one PermaSease 30-30 sample, which were from past production of these products. These samples were received in 30-ml polypropylene containers, under chain of custody and in good condition with the original seals intact, on June 7 and July 8, 2021 from Tom Philips (State Chemist from MDA). According to the MDA, these samples have been stored at their location for approximately two years, unopened and under controlled, ambient conditions. In addition, one empty unused (new, never used) sample container (polypropylene, 30-ml) was received from MDA on July 8, 2021.

The ACB also received three (3) samples of Permanone 30-30 directly from the manufacturer, Bayer Crop Science (Bayer), on May 24, 2021, which were analyzed for comparative purpose with the MDA samples. These three Permanone 30-30 samples were collected from different stages of a May 2021 production and storage line: one sample was directly off the production line (exposed to manufacturing machinery only), one sample was from a 275-gallon storage container, and one was an unopened 5-gallon end-user container (this sample was first stored in the 275-gallon container and then transferred to a 5-gallon container, which is the commercial packaging). One additional Permanone 30-30 sample was received from Bayer on July 2, 2021. This additional Permanone 30-30 sample (Permanone 30-30 retained) has a production date nine (9) days after the production of the Permanone 30-30 products received from MDA.

Along with the product samples, for control blanks, the ACB received from MDA an unused 30-ml polypropylene sample container; and from Bayer, a mineral oil sample and an unused 5-gallon metal sample container with a plastic lid. **Table 1** details all samples received and analyzed by the ACB. The samples were stored in a secured sample storage room at the ACB laboratory until analysis.

Table 1. List of the samples received and analyzed.

Product /samples	Source	ID	Receiving date	Lot #
PermaSease 30-30	MDA	SN 14156	6/7/2021	Not available
Permanone 30-30	MDA	SN 14157	6/7/2021	NT65KX0607
Permanone 30-30	MDA	SN 14158	7/8/2021	NT65KX0607
30 ml sample container	MDA	SN 14158 blank control	7/8/2021	
Mineral oil	Bayer	Production field blank	5/24/2021	
Permanone 30-30	Bayer	Production Line	5/24/2021	NT57MX0491 [*]
Permanone 30-30	Bayer	From 275-gal container	5/24/2021	NT57MX0491 [*]
Permanone 30-30	Bayer	From 5-gal container	5/24/2021	NT57MX0491 [*]
5-gal container	Bayer	Container	5/24/2021	
Permanone 30-30 Retained	Bayer	Retained	7/2/2021	NT65KX0613 ^{**}

^{*} - Lot was produced in May 2021.

^{**} - Lot was produced 9 days after MDA sample with Lot # NT65KX0607.

SAMPLE PROCESSING AND ANALYSIS

The method used for sample processing and analysis was developed and validated at the ACB and is described in **Appendix I**. Briefly, oily samples are passed through a Florisil solid phase extraction (SPE) cartridge and the oily matrix is washed off the SPE cartridge by a mixed solvent of hexane and ethyl acetate (9/1, v/v). The PFAS analytes are eluted from the SPE cartridge with a methanol/acetone mixture (9/1, v/v). The collected eluate samples are concentrated and analyzed with an LC-MS/MS under negative Electro Spray Ionization mode (ESI). The instrumental analysis of the samples with LC-MS/MS essentially follows the procedure described in EPA Method 537.1. Isotopically labeled internal standards are used for quantitation. Isotopically labeled extraction standards are added prior to sample processing and the recoveries from each sample are monitored. Method limits of quantification (LOQs) are 0.025 ng/g (or ppb) for most of the analytes, and the method limit of detection (LOD) is estimated to be 0.008 ppb. For an analyte to be positively identified in the sample when monitoring with LC-MS/MS, the following

conditions must be met: 1) measured values must be above LOD, 2) confirmation mass transition(s) must be present if they are available, and 3) the analyte must be present in all duplicate samples. Detailed information on the method validation can be provided upon request.

To further reduce the possibility of false positives due to the complex matrices of these samples, a Q-Exactive™ HF HRAM LC-MS was used to confirm the identification of the PFAS analytes. The Q-Exactive™ HRAM LC-MS was operated under negative ESI mode and the data was acquired using Full MS and ddMS2 methods.

RESULTS AND DISCUSSION

LC-MS/MS analysis: Using the method as described in **Appendix I**, the only PFAS compound initially identified in the three MDA samples (PermaSease 30-30 and duplicate samples of Permanone 30-30) is PFHpA at 0.042 ppb, 0.169 ppb and 0.184 ppb respectively. Similarly, only PFHpA was identified in the Bayer retained Permanone 30-30 sample (received on July 2, 2021), but the level was below the quantitation limit (LOQ of 0.025 ppb). PFAS was not detected in any of the three (3) Permanone 30-30 samples from a May 2021 production (received from Bayer on May 24, 2021), nor in the mineral oil production field blank. All sample containers (received from MDA and Bayer) are also free of target analytes.

Results from laboratory quality control samples processed at the same time met ACB's acceptance criteria. No PFAS was detected in the procedural blanks. The recoveries of PFAS from laboratory spiked control blanks and matrix spike samples were within the acceptance criteria established during the method validations.

Q-Exactive™ HRAM LC-MS analysis: Further analysis of the three product samples from MDA and the Bayer retained sample, using Q-Exactive™ HRAM LC-MS (see **Appendix I**), did not confirm the presence PFHpA. Results of various positive and negative control samples were consistent between findings on the HRAM LC-MS and the LC-MS/MS. The PFHpA peak identified in the LC-MS/MS analysis is, therefore, believed to be a false positive resulting from possible matrix interference.

It is worth noting that the extracts of the Bayer samples from the May 2021 production (received on May 24, 2021) were colorless. However, the extracts of the MDA samples and of the Bayer retained sample – all of which were in storage for approximately two years – showed visible discoloration (brownish color).

Table 2 lists the results for the product samples received from the MDA; **Table 3**, for the product samples received from Bayer; and **Table 4**, for the rinsates from the unused sample containers from MDA and Bayer, and for the production field blank from Bayer. The full analyte names and CAS numbers are listed in **Appendix II**.

Table 2. Results of product samples from MDA (values, if listed, are in ppb or ng/g).

DATE RECEIVED	6/7/2021	6/7/2021	7/8/2021
DATE ANALYZED	6/8/2021, 6/15/2021	6/8/2021, 6/15/2021	7/8/2021
	SN 14156 PermaSease 30-30	SN 14157 Permanone 30-30	SN14158 Permanone 30-30
ANALYTE			
PFBA	ND	ND	ND
PFBS	ND	ND	ND
PFPeA	ND	ND	ND
PFPeS	ND	ND	ND
PFHxA	ND	ND	ND
PFHxS	ND	ND	ND
PFHpA	ND	ND	ND
PFHpS	ND	ND	ND
PFOA	ND	ND	ND
PFOS	ND	ND	ND
PFNA	ND	ND	ND
PFNS	ND	ND	ND
PFDA	ND	ND	ND
PFDS	ND	ND	ND
PFUdA	ND	ND	ND
PFDoA	ND	ND	ND
PFDoS	ND	ND	ND
PFTTrDA	ND	ND	ND
PFTeDA	ND	ND	ND
PFHxDA	ND	ND	ND
PFODA	ND	ND	ND
FOSAA	ND	ND	ND
N-MeFOSAA	ND	ND	ND
N-EtFOSAA	ND	ND	ND
HFPO-DA	ND	ND	ND
NaDONA	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND
11Cl-PF3OUdS	ND	ND	ND

ND = Not Detected at or above the LOD (0.008 ppb)

Table 3. Results of product samples from Bayer (values, if listed, are in ppb or ng/g).

DATE RECEIVED	5/24/2021	5/24/2021	5/24/2021	7/2/2021
DATE ANALYZED	5/25/2021, 6/2/2021	5/25/2021, 6/2/2021	5/25/2021, 6/2/2021	7/8/2021
	Production line	From a 275-gal container	From a 5-gal container	Bayer Retained
	Permanone 30-30	Permanone 30-30	Permanone 30-30	Permanone 30-30
ANALYTE				
PFBA	ND	ND	ND	ND
PFBS	ND	ND	ND	ND
PFPeA	ND	ND	ND	ND
PFPeS	ND	ND	ND	ND
PFHxA	ND	ND	ND	ND
PFHxS	ND	ND	ND	ND
PFHpA	ND	ND	ND	ND
PFHpS	ND	ND	ND	ND
PFOA	ND	ND	ND	ND
PFOS	ND	ND	ND	ND
PFNA	ND	ND	ND	ND
PFNS	ND	ND	ND	ND
PFDA	ND	ND	ND	ND
PFDS	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND
PFDoS	ND	ND	ND	ND
PFTrDA	ND	ND	ND	ND
PFTeDA	ND	ND	ND	ND
PFHxDA	ND	ND	ND	ND
PFODA	ND	ND	ND	ND
FOSAA	ND	ND	ND	ND
N-MeFOSAA	ND	ND	ND	ND
N-EtFOSAA	ND	ND	ND	ND
HFPO-DA	ND	ND	ND	ND
NaDONA	ND	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND	ND
11Cl-PF3OUdS	ND	ND	ND	ND

ND = Not Detected at or above the LOD (0.008 ppb)

Table 4. Results of production field blank and rinsates from unused sample containers.

DATE RECEIVED	5/24/2021	5/24/2021	7/8/2021
DATE ANALYZED	6/2/2021	5/25/2021, 6/2/2021	7/8/2021
	5-gal container (Bayer)	Mineral oil Production field blank (Bayer)	30-ml container (MDA)
ANALYTE			
PFBA	ND	ND	ND
PFBS	ND	ND	ND
PFPeA	ND	ND	ND
PFPeS	ND	ND	ND
PFHxA	ND	ND	ND
PFHxS	ND	ND	ND
PFHpA	ND	ND	ND
PFHpS	ND	ND	ND
PFOA	ND	ND	ND
PFOS	ND	ND	ND
PFNA	ND	ND	ND
PFNS	ND	ND	ND
PFDA	ND	ND	ND
PFDS	ND	ND	ND
PFUdA	ND	ND	ND
PFDoA	ND	ND	ND
PFDoS	ND	ND	ND
PFTrDA	ND	ND	ND
PFTeDA	ND	ND	ND
PFHxDA	ND	ND	ND
PFODA	ND	ND	ND
FOSAA	ND	ND	ND
N-MeFOSAA	ND	ND	ND
N-EtFOSAA	ND	ND	ND
HFPO-DA	ND	ND	ND
NaDONA	ND	ND	ND
9Cl-PF3ONS	ND	ND	ND
11Cl-PF3OUdS	ND	ND	ND

The analytical results and the sample processing procedures have been subject to ACB internal quality assurance (QA) review. The findings and notations of the QA review are documented in the ACB QA review sheets.

APPENDICES

- I. Sample preparation and analysis of selected PFAS from oily matrices (ACB Project B21-02).
- II. Full analyte names and CAS numbers.

Appendix I -

Sample Preparation and Analysis of Selected PFAS from Oily Matrices

Section 1. SAMPLE PREPARATION

1. Measure 4 g (about 5 ml) of samples into a 15 ml polypropylene tube.
2. Prepare a procedural blank and a laboratory blank spike (LBS) samples (5 ml of hexane each).
3. Prepare a matrix spike (MS) sample with one of the samples.
4. Fortify each sample with 50 µl of extraction standards (PFAC-ES-W, 10 ng/ml, isotopically labeled PFAS standards).
5. Fortify the appropriate samples (LBS, MS) with PFAS standard (PFAC-MXC-W, 10 ng/ml, native PFAS).
6. Mix by vortex.
7. Prepare Florisil SPE (1 g) on a SPE manifold. The Florisil SPE cartridges should have non-PFTE frits (e.g., BondElut). Ensure the SPE manifold does not have PTFE valves and dripping tubes.
8. Condition the Florisil SPE by passing through 15 ml of 1% acetic acid in methanol/acetone (9/1, v/v), followed by 5 ml of hexane/ethyl acetate (9/1, v/v).
9. Load the samples on to the SPE. Apply a vacuum to the manifold to ensure the flow through the SPE is dropwise (1-2 ml/min).
10. After all the samples pass through the SPE (do not let the SPE goes to dry), rinse the sample tubes with three aliquots of 4 ml of hexane/ethyl acetate (9/1, v/v). Each time transfer the rinse solution to the SPE and let the hexane/ethyl acetate pass through the SPE. Continue to pull the vacuum to ensure all solvent has passed through (no more dripping).
11. Place 15 ml polypropylene collection tubes under the SPE. Add 10 ml of 1% of acetic acid in methanol/acetone (9/1, v/v) to each SPE and collect the eluant.
12. Remove the collected samples from the manifold and concentrate to dryness/near dryness under a stream of N₂ in a water bath (40-50°C).
13. Add 50 µl of internal standard (PFAC-IS-W, 10 ng/ml) to each sample.
14. Add about 400 µl of 0.1% acetic acid in methanol/water (9/1, v/v) to each sample and vortex.
15. Transfer the samples to polypropylene autosampler vials with polyethylene caps for instrumental analysis, either by liquid chromatography tandem mass spectrometer (LC-MS/MS) (**Section 2.**) or by high resolution accurate mass (HRAM) mass spectrometer coupled with liquid chromatography (HRAM LC-MS, **Section 3.**)
16. A 0.2 µm nylon syringe filter may be used if samples look cloudy and need filtration.

SECTION 2. SAMPLE ANALYSIS by LC-MS/MS

Calibration Standards

Standard materials were purchased from commercial sources. Calibration standards are made in methanol/water (95/5, v/v, with 0.1% acetic acid) in the range of 0.02 ng/ml to 20 ng/ml. Prepared calibration standards contain all native, extraction standard and internal standard analytes.

Instrument Analysis

Sample analysis is performed with a liquid chromatography tandem mass spectrometer (LC-MS/MS), following EPA method 537.1 “*Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC-MS/MS)*”.

A Waters Acquity BEH C₁₈ column (2.1 mm x 100 mm, 1.7 µm) and a gradient of 5 mM ammonium acetate aqueous solution / 5 mM ammonium acetate in acetonitrile mobile phases were used for compound separation. The plumbing of the LC has been replaced with PEEK tubing. A short trap column is placed between the pump head and autosampler valve. Mass spectrometer is operated under ESI- multiple reaction monitoring mode. Instrument parameters for LC and MS/MS are listed in **Table 1** and **Table 2**, respectively. Monitored MS transitions are listed in **Table 3**.

Table 1. LC Instrument Parameters.

LC			
Column	Waters Acquity BEH C18 column (2.1 mm x 100 mm, 1.7 µm)		
Injection Volume	20 µL		
Column Temp.	35°C		
Flow rate	300 µL/min.		
Mobile Phases & Gradient	Time (min.)	5 mM ammonium acetate in water	5 mM ammonium acetate in acetonitrile
	0	90%	10%
	4	75%	25%
	6	50%	50%
	11	5%	95%
	15	5%	95%
	17	90%	10%
	22	90%	10%

Table 2. MS/MS Instrument Parameters

MS/MS	
Polarity	Negative
Ionization	ESI
Scan type	MRM
Curtain gas	30 psi
Ionspray voltage	-4,500 V
Nebulizer current	2.85 μ A
Source temperature	450°C
Ion source gas 1	45 psi
Ion source gas 2	40 psi

Table 3. Analyte Monitored MS Transitions.

Compound	Parent mass	Product mass	DP	CE	CXP
Natives					
PFBA	213	169	-40	-14	-17
PFBS	299	80	-70	-66	-9
	299	99	-70	-36	-11
PFPeA	263	219	-25	-12	-11
PFPeS	349	80	-80	-72	-9
	349	99	-80	-38	-11
PFHxA	313	269	-15	-14	-11
	313	119	-15	-26	-15
PFHxS	399	80	-75	-90	-9
	399	99	-75	-78	-11
PFHpA	363	319	-60	-14	-55
	363	169	-60	-24	-19
PFHpS	449	80	-115	-102	-19
	449	99	-115	-86	-11
PFOA	413	369	-5	-14	-9
	413	169	-5	-22	-17
PFOS	499	80	-80	-108	-9
	499	99	-80	-60	-11
PFNA	463	419	-35	-14	-21
	463	219	-35	-24	-13

Compound	Parent mass	Product mass	DP	CE	CXP
PFNS	549	80	-85	-120	-9
	549	99	-85	-112	-13
PFDA	513	469	-45	-16	-27
	513	269	-45	-26	-33
PFDS	599	80	-65	-132	-9
	599	99	-65	-116	-11
PFUdA (PFUnA)	563	519	-40	-16	-27
	563	169	-40	-30	-15
PFDoA	613	569	-30	-32	-27
	613	169	-30	-18	-15
PFDoS	699	80	-40	-168	-21
PFTrDA	663	619	-50	-18	-31
	663	169	-50	-36	-19
PFTeDA	713	669	-50	-18	-33
	713	169	-50	-34	-17
PFHxDA	813	769	-60	-22	-27
PFODA	913	869	-20	-15	-15
FOSAA	556	498	-65	-44	-29
N-MeFOSAA	570	419	-20	-26	-23
	570	483	-20	-24	-35
N-EtFOSAA	584	419	-30	-30	-25
	584	483	-30	-24	-39
HFPO-DA	329	169	-15	-18	-15
	329	285	-15	-8	-17
NaDONA	377	251	-30	-16	-13
	377	85	-30	-34	-9
9Cl-PF3ONS	531	351	-50	-36	-19
	531	99	-50	-76	-11
11Cl-PF3OUdS	631	451	-50	-40	-25
	631	83	-50	-86	-9

Extraction Standards					
Compound	Parent mass	Product mass	DP	CE	CXP
M2PFTeDA	715	670	-35	-18	-55
M3PFBS	302	99	-60	-36	-15
M3PFHxS	402	99	-65	-74	-11
M5PFPeA	268	223	-50	-22	-13
M6PFDA	519	474	-25	-14	-27
M7PFUdA	570	525	-25	-16	-13
M8PFOA	421	376	-20	-12	-45
M8PFOS	507	80	-50	-110	-9
M9PFNA	472	427	-25	-14	-27
MPFBA	217	172	-60	-14	-15
MPFDoA	615	570	-35	-18	-39
M NMeFOSAA	573	419	-45	-28	-11
M NEtFOSAA	589	419	-5	-28	-23
M3HFPO-DA	332	287	-5	-8	-17
Internal Standards					
M3PFBA	216	172	-35	-6	-11
MPFDA	515	470	-40	-16	-27
M2PFOA	415	370	-20	-14	-21
MPFOS	503	99	-10	-106	-41
	503	80	-10	-110	-9

Quantitation is based on internal standard method. The recoveries of the isotopically labelled extraction standards from each sample, in addition to the recoveries of spiked compounds from LBS and matrix spike, are monitored.

SECTION 3. SAMPLE ANALYSIS by HRAM LC-MS

This is an alternative instrumental method for analysis of the perfluoroalkyl substances (PFAS), as compared with the traditional technique using LC-MS/MS and can be used to confirm presence of PFAS at low levels (around or below 10 times the LC-MS/MS reported limits of quantitation). Equivalent analytical columns and materials may be used in place of those described in this method. The instrument parameters may be modified to enhance the performance of the method.

Calibration Standards (same as that in Section 2)

Standard materials were purchased from commercial sources. Calibration standards are made in methanol/water (95/5, v/v, with 0.1% acetic acid) in the range of 0.02 ng/ml to 20 ng/ml. Prepared calibration standards contain all native, extraction standard and internal standard analytes.

Instrument Analysis

Sample analysis is performed with a Q-Exactive™ HF high resolution accurate mass (HRAM) mass spectrometer coupled with liquid chromatography.

A Thermo Hypersil GOLD column (2.1 mm x 100 mm, 1.9 µm particle size) and a gradient of 5 mM ammonium acetate aqueous solution / 5 mM ammonium acetate in acetonitrile mobile phases were used for compound separation. A short trap column (Waters XBridge C₁₈ 3.5 µm, 2.1mm x 50 mm) is placed between the pump head and autosampler. Mass spectrometer is operated in negative ESI mode and the data were acquired using Full MS and ddMS² methods. Instrument parameters for LC and MS/MS are listed in **Table 4** and **Table 5**, respectively. Quantitation and confirmation masses are listed in **Table 6**.

Table 4. LC Parameters.

Column	Thermo Hypersil GOLD column (2.1 mm x 100 mm, 1.9 µm particle size)		
Injection Volume	5 µL		
Column Temp.	40°C		
Flow rate	300 µL/min.		
Mobile Phases & Gradient	Time (min.)	5 mM ammonium acetate in water	5 mM ammonium acetate in acetonitrile
	0	95%	5%
	9	5%	95%
	10	0%	100%
	13	0%	100%
	13.5	95%	5%
	17	95%	5%

Table 5. HRAM MS Instrument Parameters.

Ionization	ESI Negative
Scan type	Full MS and ddMS ²
Resolution	60,000
Inclusion	On
ddMS ²	Top 5
Sheath gas flow	48
Aux gas flow	11
Spray voltage	3
Capillary temperature	260
S-lens	60
Aux gas temperature	410

Table 6. Masses used in quantitation and confirmation.

Compound	m/z	m/z	m/z
Natives			
PFBA	212.9787	168.9885	
PFBS	298.9429	79.9561	
PFPeA	262.9760	218.9857	
PFPeS	348.9398	79.9550	
PFHxA	312.9730	268.9830	
PFHxS	398.9366	79.9546	
PFHpA	362.9699	318.9799	296.9780
PFHpS	448.9335	449.9360	79.9550
PFOA	412.9667	368.9767	
PFOS	498.9307		
PFNA	462.9636	418.9737	428.1716
PFNS	548.9274		
PFDA	512.9602	468.9703	
PFDS	598.9244		
PFUdA (PFUnA)	562.9572	518.9672	563.9606
PFDoA	568.9642	612.9542	
PFDoS	698.9182		
PFTTrDA	662.9513	618.9610	663.9550
PFTeDA	712.9483	168.9886	668.9580
PFHxDA	812.9421	768.9515	
PFODA	912.9340	868.9441	

FOSAA	555.9520		
N-MeFOSAA	569.9678		
N-EtFOSAA	583.9836		
HFPO-DA	328.9680	284.9780	168.9885
NaDONA	376.9690	250.9760	84.9892
9Cl-PF3ONS	530.8975	350.1258	
11Cl-PF3OUdS	630.8899	632.8868	

Extraction Standards

M2PFTeDA	714.9548	
M3PFBS	301.9531	
M3PFHxS	401.9467	
M4PFHpA	366.9831	321.9900
M5PFHxA	317.9897	272.9966
M5PFPeA	267.9928	222.9991
M6PFDA	518.9803	473.9872
M7PFUdA	569.9807	524.9872
M8PFOA	420.9935	376.0002
M8PFOS	506.9570	
M9PFNA	471.9936	427.0003
M4PFBA	216.9923	171.9986
MPFDoA	614.9609	569.9677
M NMeFOSAA	572.9867	
M NEtFOSAA	589.0150	
M3HFPO-DA	286.9848	331.9780

Internal Standards

M3PFBA	215.9888	171.9987
MPFDA	514.9670	469.9738
M2PFOA	414.9733	369.9800
MPFOS	502.9439	

Identifications are based on the retention times and accurate masses. Quantitation is based on internal standard method. The recoveries of the isotopically labelled extraction standards from each sample, in addition to the recoveries of spiked compounds from laboratory blank spike (LBS) and matrix spike (MS), are monitored.

APPENDIX I -

CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS and CHEMICAL NAMES

Analyte	CAS #	Name
PFBA	375-22-4	Perfluorobutanoic Acid
PFBS	375-73-5	Perfluorobutanesulfonic Acid
PFPeA	2706-90-3	Perfluoropentanoic Acid
PFPeS	2706-91-4	Perfluoropentanesulfonic Acid
PFHxA	307-24-4	Perfluorohexanoic Acid
PFHxS	355-46-4	Perfluorohexanesulfonic Acid
PFHpA	375-85-9	Perfluoroheptanoic Acid
PFHpS	375-92-8	Perfluoroheptanesulfonic Acid
PFOA	335-67-1	Perfluorooctanoic Acid
PFOS	1763-23-1	Perfluorooctanesulfonic Acid
PFNA	375-95-1	Perflurononanoic Acid
PFNS	68259-12-1	Perfluorononanesulfonic Acid
PFDA	335-76-2	Perfluorodecanoic Acid
PFDS	335-77-3	Perfluorodecanesulfonic Acid
PFUdA	2058-94-8	Perfluoroundecanoic Acid
PFDoA	307-55-1	Perfluorododecanoic Acid
PFDoS	79780-39-5	Perfluorododecanesulfonic Acid
PFTTrDA	72629-94-8	Perfluorotridecanoic Acid
PFTeDA	376-06-7	Perfluorotetradecanoic Acid
PFHxDA	67905-19-5	Perfluorohexadecanoic Acid
PFODA	16517-11-6	Perfluorooctadecanoic Acid
FOSAA	2806-24-8	Perfluorooctane sulfonamidoacetic Acid
N-MeFOSAA	2355-31-9	N-Methyl Perfluorooctane sulfonoamidoacetic Acid
N-EtFOSAA	2991-50-6	N-Ethyl Perfluorooctane sulfonoamidoacetic Acid
HFPO-DA	13252-13-6	Hexafluoropropylene oxide dimer acid
NaDONA	958445-44-8	Sodium dodecafluoro-3H-4,8-dioxanonanoate
9Cl-PF3ONS	756426-58-1	9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid
11Cl-PF3OUdS	763051-92-9	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid